



Certificate of Analysis

Standard Reference Material[®] 656

Silicon Nitride Powders for Quantitative Analysis by Powder Diffraction

This Standard Reference Material (SRM) consists of two powders intended for quantitative analysis of the α and β polymorphs of silicon nitride via powder diffraction methods. The powders are combinations of the α and β polymorphs; one is high in the α phase content (α 656), while the other contains a larger amount of the β polymorph (β 656). This selection allows the user to choose the powder which is optimal for their specific analysis. A unit of SRM 656 consists of approximately 10 g of each powder.

Material Description: The powders consist of sub-micrometer, equi-axial, non-aggregated grains that do not display the effects of extinction or preferred orientation. The powders were bottled in an argon atmosphere; silicon nitride is known to slowly react with atmospheric moisture.

An analysis of the quantitative results from Rietveld analyses of X-ray powder diffraction data indicated that the SRM material was homogeneous with respect to diffraction properties.

Certified Values and Uncertainty: The certified phase compositions, expressed as a mass fraction are given in Table 1.

Table 1. α 656 (High α Phase Powder)

Phase	Mass	Uncertainty
α	87.5 %	± 0.59 %
β	3.0 %	± 0.05 %
Amorphous	9.5 %	± 0.61 %

β 656 (High β Phase Powder)

α	16.3 %	± 0.81 %
β	75.1 %	± 2.54 %
Amorphous	8.6 %	± 0.60 %

Each interval defined by a certified value and its uncertainty in this certificate is a 95 % confidence interval for the true value of the mean in the absence of systematic error [1,2].

Expiration of Certification: The certification of this SRM is valid indefinitely within the stated uncertainties, provided the SRM is stored and handled in accordance with the "Storage" section of this certificate.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

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See Certificate Revision History on Last Page

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The material preparation, measurements and data analyses leading to the certification of this SRM were provided by J.P. Cline of the NIST Ceramics Division and R.B. Von Dreele of Argonne National Laboratory, Argonne, IL. Supplemental characterization was performed by M.D. Vaudin and D.B. Minor of the NIST Ceramics Division.

Statistical analysis was provided by S.B. Schiller and L.M. Oakley of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Materials: The powder used for α 656 was UBE E10, UBE Industries Ltd., Tokyo, Japan¹, while that used for β 656 was Denka SN-P21FC, Denki Kagaku Kogyo K.K., Tokyo, Japan. The high β phase content powder was donated to NIST by Denki Kagaku Kogyo K.K. We also acknowledge the cooperation of UBE Industries Ltd.

Certification: This SRM was certified in 1995 with respect to the mass fraction of the α and β polymorphs of Si_3N_4 that exhibited Bragg scattering in correspondence to that of crystalline components, or phase composition and phase purity. The certification procedure utilized Quantitative Rietveld Analyses (QRA) [3] (for a complete discussion of the Rietveld method, see [4,5]) of neutron time-of-flight (TOF) diffraction measurements in conjunction with the use of SRM 676 [6] as the internal standard. This procedure referenced the phase purity of SRM 656 against that of SRM 676. The basis of the method rests on an analysis of the discrepancy between the results of powder diffraction experiments, which measure the mass of material exhibiting Bragg diffraction, relative to weighing operations, which include all components. The phase purity of SRM 656, as certified in 1995, reflected our approximate knowledge of the phase purity of SRM 676 in 1995 [7]; however, SRM 676 was certified with respect to phase purity in 2005. Therefore, the certified phase purity of SRM 656 was revised in 2005.

A long-count-time X-ray powder diffraction pattern of a given powder sample may offer data consistent with a high purity powder, i.e., no impurity phases and a background that is consistent with contributions of air scatter from the incident beam and thermal diffuse scatter from the sample. However, the surface region of any crystalline material will not diffract as the bulk due to relaxation of the crystal structure and inclusion of surface reaction products. While this surface layer may only be on the order of a few crystallographic units in thickness, in a finely divided solid it can easily account for several percent of the total mass. The characterization of “phase purity” or “amorphous content” discussed herein is not in the context of a mechanically separable impurity phase, but it is a microstructural characteristic innate to the chemistry of Si_3N_4 and the production history of the SRM feedstock.

The QRA of laboratory, divergent beam X-ray powder diffraction (XRPD) data displayed a systematic bias of less than 2 %; however, these results were as precise as those determined from the TOF data. Therefore, the certified phase composition was determined from the TOF data while the homogeneity of the SRM material was verified with Rietveld analyses of XRPD data. It should be noted that the mechanism inducing this bias is not operative in Reference Intensity Ratio (RIR) based methods [8] (for a complete discussion of RIR methods, see [9]). The reported, non-certified, lattice parameters were from the aforementioned Rietveld analyses of the XRPD data. While the XRPD data suffer from centration and penetration errors and, therefore, are not metrological in nature; a linkage is nonetheless established between the reported lattice parameters and the X-ray emission spectrum of Cu, establishing a qualified traceability to the International System of Units (SI) [10].

Five randomly selected samples from each of the two SRM materials were admixed with a known amount of SRM 676 for TOF neutron diffraction analysis. TOF data were obtained on the High Intensity Powder Diffractometer (HIPD) at the Manuel Lujan, Jr., Neutron Scattering Center (LANSCE), Los Alamos, NM. The samples were contained in 9.5 mm diameter by 50 mm long vanadium cans during the analysis. Each sample was exposed to the neutron beam for 1.68 h to 6.13 h with the LANSCE source operating at approximately 60 μA proton beam current. Data used for this certification were obtained from detector banks positioned at $\pm 153^\circ 2\theta$, each covering a d-spacing range of 0.04 nm to 0.48 nm. Rietveld refinements using the General Structure Analysis System (GSAS) [11] of the three phases in these samples included: scale factors for each phase, lattice parameters, atomic positional and thermal parameters, and crystallite size and microstrain [12] parameters for the majority phases (alumina and α silicon nitride in the high α material, and alumina and β silicon nitride in the high β material), an absorption factor and six terms of a background function describing the effects of thermal diffuse and incoherent scattering for each data set.

¹ Certain commercial materials and equipment are identified in order to adequately specify the experimental procedure. Such identification does not imply a recommendation or endorsement by NIST, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

X-ray diffraction data for homogeneity testing and lattice parameter determination were collected on two specimens removed from each of ten randomly selected bottles of both SRM materials. These ten bottles included those from which the TOF specimens were prepared. These specimens also had known amounts of SRM 676 admixed with them. These XRPD data were collected on a Siemens D500 diffractometer equipped with a focusing Ge incident beam monochromator, sample spinner and a scanning position sensitive detector. Copper $K\alpha_1$ radiation, $\lambda = 0.154\,059\,45\text{ nm}$ [13], was used. The scan range was from 17.5° to $152^\circ\,2\theta$. GSAS was used for a Rietveld refinement of the three phases. Refined parameters included: scale factors, crystallite size and strain induced broadening terms of the pseudo-Voigt profile function [14], lattice parameters, sample shift and transparency terms, atomic thermal and position parameters for the silicon, aluminum and oxygen atoms, Lorentz polarization factor and six terms of a background function describing the effects of thermal diffuse scattering and air scattering (incoherent) of the incident beam. Gaussian U, V and W terms [15] were presumed to be instrumental in origin and fixed at those obtained from a refinement of SRM 660 [16,17].

The relative intensities of the high intensity lines from the two SRM powders, and the RIR of silicon nitride (SRM 656), were certified as follows: XRPD data were collected from suites of five samples of unadulterated SRM material in the case of the relative intensity measurements, a third suite of five samples consisted of 50:50 mixtures of the two SRM materials for determination of the RIR. These data were collected using $\text{CuK}\alpha$ radiation and fixed divergence slits on a Siemens D5000 diffractometer equipped with a sample spinner, graphite post monochromator and scintillation detector. The intensities were determined by fitting a split Pearson VII profile function to the raw data using the profile analysis software SHADOW². Constraints were used on some of the profile shape parameters in order to obtain the most realistic fitting of the overlapped profiles. The relative intensity data include the “relative intensity” of the peaks from the minor phase as well as the major phase from each powder. The scaling of these intensities is against the 100 % line of the major phase. The RIR data was biased using the certified quantitative data to result in a value which corresponded to a true 50:50 mixture of the α and β phases.

The XRPD data from the high β phase powder of SRM 656 was found to display the effects of planar faults perpendicular to the c axis. The presence of these faults, confirmed by Transmission Electron Microscopy (TEM), lead to an anisotropic profile broadening, which affected reflections from planes intersecting the c axis; prismatic reflections were unaffected. A TEM examination of the high α material indicated it was free of such defects. These faults have, in turn, led to a greater uncertainty associated with the certification data from the high β phase powder. Examination of the certified relative intensity data confirm that the uncertainty associated with measurements of the 011 reflection from the high β phase material is unduly large. The basing of a quantitative analysis on this reflection alone is not recommended.

Table 2. Certified Relative Intensity Data from the Two Silicon Nitride Powders of SRM 656

Phase	2θ	h k l	Relative Intensity (α 656)	Uncertainty	Relative Intensity (β 656)	Uncertainty
α	20.59	1 0 1	100.00	0.00	13.41	± 0.39
α	22.92	1 1 0	45.11	± 0.59	5.43	± 0.18
β	23.38	1 1 0	1.08	± 0.21	35.26	± 0.34
α	26.53	2 0 0	32.54	± 0.63	3.73	± 0.40
β	27.07	0 2 0	3.87	± 0.23	100.00	0.00
α	31.01	2 0 1	97.68	± 0.68	12.72	± 0.73
α	31.82	0 0 2	11.81	± 1.09	0.95	± 0.10
β	33.68	0 1 1	4.09	± 0.11	89.70	± 3.22
α	34.58	1 0 2	82.68	± 0.22	11.33	± 0.61
α	35.34	2 1 0	97.88	± 1.33	12.16	± 0.59
β	36.06	1 2 0	5.38	± 0.38	97.45	± 0.86

The certified Reference Intensity Ratio $\text{RIR}_{\alpha/\beta}$ of SRM 656 is 0.713 ± 0.015 .

² Materials Data, Inc., PO Box 791, Livermore, Ca. 94551-0791

Storage: SRM 656 was bottled under argon to protect against humidity. Silicon nitride is known to react slowly with atmospheric moisture. When not in use, store the unused portion of this powder tightly capped in the original bottle or in a manner with similar or greater protection against humidity, such as a desiccator.

Information Values and Uncertainties: NIST information values are considered to be of interest to the SRM user, but are not certified because the measurements are not traceable to the SI, or only a limited number of analyses were performed which disallowed imparting plausible uncertainties to the measured values. The information values for lattice parameters, as determined from the aforementioned Rietveld analysis of the XRPD data, and the particle size distribution, as determined by laser scattering, are given in Table 3 and 4, respectively. The interval defined by a value and its uncertainty is a 95 % confidence interval for the true value of the mean in the absence of systematic error. Additional data on elemental and chemical impurities of this SRM have been published in reference [18].

Table 3. Lattice Parameters of SRM 656 Powders

Material	Phase	a (nm)	Uncertainty	c (nm)	Uncertainty
α 656	α	0.775 263 0	$\pm 0.000\ 007\ 7$	0.561 937 2	$\pm 0.000\ 006\ 3$
	β	0.760 533 0	$\pm 0.000\ 020\ 0$	0.290 637 1	$\pm 0.000\ 009\ 5$
β 656	α	0.775 094 5	$\pm 0.000\ 006\ 4$	0.561 866 1	$\pm 0.000\ 006\ 9$
	β	0.760 229 3	$\pm 0.000\ 007\ 2$	0.290 682 7	$\pm 0.000\ 002\ 6$

Table 4. Typical Particle Size Data by Laser Scattering Method

Particle Size (μm)	Cumulative Mass Fraction Finer Than	
	α 656	β 656
0.3	0.3 %	4.5 %
0.6	20.8 %	43.5 %
0.9	48.6 %	66.8 %
1.2	64.2 %	78.4 %
1.5	76.2 %	85.9 %
1.8	85.2 %	90.9 %
2.1	91.3 %	94.1 %
2.4	95.0 %	96.2 %
2.7	97.2 %	97.6 %
3.0	98.5 %	98.5 %
4.0	99.8 %	99.6 %
5.0	100.0 %	100.0 %

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Certificate Revision History: 20 September 2005 (This revision reflects a change in the certified values for phase composition resulting from the improved characterization of phase purity as provided in SRM 676); 30 March 1995 (Original certificate date).
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Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; email srminfo@nist.gov; or via the Internet at <http://www.nist.gov/srm>.